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## PATENT SPECIFICATION

DRAWINGS ATTACHED

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## COMPLETE SPECIFICATION

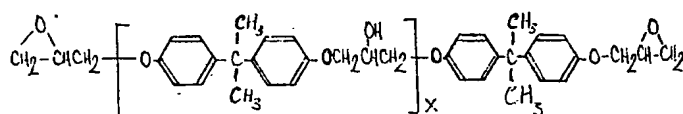
New Epoxy Ethers, their preparation and Cured Products  
obtained therefrom

We, SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ N.V., a company organised under the laws of the Netherlands, of 30 Carel van Bylandtlaan, The Hague, The Netherlands, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

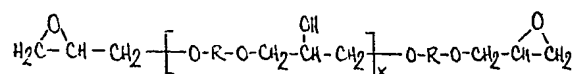
This invention relates to new epoxy ethers of substituted polyhydric phenols, to their preparation and utilization, particularly in the formation of valuable cured products.

Epoxy ethers of unsubstituted polyhydric phenols, such as glycidyl ethers of 2,2-bis(4-hydroxyphenyl)propane, have been in commercial use for some time. They find wide use in the preparation of surface coatings, adhesives, mouldings and castings and the like. These materials, however, have certain disadvantages which have limited their applications. It has been found, for example, that considerable time is required to cure the resins at the lower temperatures. This prevents their use for certain types of coatings, such as those to be applied to roads, and the like. In addition, the cured resins do not have the heat resistance required for the new applications in missiles and rocketry.

According to the invention we provide, as new compounds, a polyglycidyl ether of the formula:

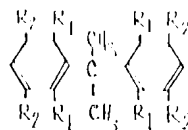


wherein x is an integer from 0 to 10 and at least one of the p-phenylene radicals is substituted with a methylol group, no other substituents being present. Preferably x is from 0 to 5. Preferably the polyglycidyl ether has from 1-4 methylol groups per molecule. Preferred glycidyl ethers are represented by the formula:

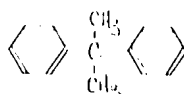


wherein R is a bivalent

[Price 4s. 6d.]



group wherein  $R_1$  and  $R_2$  are hydrogen or methylol groups and  $x$  is a number from 0 to 10 with the proviso that in at least one  $R_1$  at least one  $R_2$  is a methylol group, and particularly preferred are compounds of the above formula wherein  $x$  is a number from 0 to 5 and each  $R$  is a methylol substituted



group

The new glycidyl ethers of the present invention may be exemplified by the following:

diglycidyl ether of 2 - (3 - methylol - 4 - hydroxyphenyl) - 2 - (4 - hydroxyphenyl)propane, diglycidyl ether of 2,2 - bis(3 - methylol - 4 - hydroxyphenyl)propane, diglycidyl ether of 2,2 - bis(3,5 - dimethylol - 4 - hydroxyphenyl)propane.

It has been found that these new glycidyl ethers have quite different properties from the unsubstituted epoxy ethers and meet many of the present needs of the epoxy resin industry. It has turned out, for example, that these epoxy ethers have surprisingly fast reaction at low temperatures, particularly in combination with polyamines, and can be cured with these materials at a rate which is from 4 to 10 or more times faster than the conventional epoxy resins. The surprising property permits the new epoxy ethers to be used for a wide variety of different applications, particularly in the coating and surface industries. In addition, it has been found that the cured products obtained by reacting the new epoxy ethers with curing agent, and particularly the aromatic polyamine curing agent, have unexpectedly high heat distortion points. The heat distortion points in many cases are from 50°C to 150°C higher than those obtained under similar conditions with the unsubstituted glycidyl ethers. This surprising property permits the new epoxy ethers to be used for important casting and moulding operations and in the formation of reinforced composites, such as in the filament winding and laminating industries.

The new glycidyl ethers of the invention can be prepared by reacting a 2,2-bis(4-hydroxyphenyl)propane substituted on an aromatic ring with as only substituent at least one methylol group per molecule with epichlorohydrin or  $\alpha$ -dichlorohydrin in a mole ratio of at least 1 : 1.1 in the presence of an alkaline material. The formation of the new epoxy ethers in this manner was surprising in that it was expected that the methylol group would react with the epoxy-forming material and would not remain as such. However, surprisingly, high yields of the desired epoxy ether with the methylol group or groups unreacted were obtained by this new technique.

Examples of the above-described methylol-substituted phenols are 2 - (3 - methylol - 4 - hydroxyphenyl) - 2 - (4 - hydroxyphenyl)propane; 2,2 - bis - (3 - methylol - 4 - hydroxyphenyl)propane; and 2,2 - bis(3,5 - dimethylol - 4 - hydroxyphenyl)propane. These methylol-substituted phenols can be prepared by reacting 2,2 - bis(4 - hydroxyphenyl)propane with formaldehyde, preferably used as a 37% aqueous formaline solution, in the presence of an alkaline catalyst, such as sodium hydroxide, at temperatures ranging preferably from room temperature to 100°C. The formaldehyde and phenol are preferably combined in such quantities as to furnish approximately on mol up to 5—10% excess of formaldehyde for every ring carbon atom to be reacted. Thus, the mono-methylol-substituted products are obtained by the use of the reactants on a mol per mol basis, while the dimethylol-substituted products are obtained by using 2 mols of formaldehyde per mol of the phenol.

Solvents such as methanol, ethanol, water-alcohol mixtures, ketones and the like may be used in the reaction, for example, in amounts from 10 to 60% by weight of

the reactants. After the reaction the alkaline catalyst can be neutralized by the addition of an acid, such as dilute sulphuric acid or dilute hydrochloric acid, and the solvent can be removed by distillation.

The reaction of the methylol-substituted 2,2 - bis(4 - hydroxyphenyl)propane with epichlorohydrin or  $\alpha$  - dichlorohydrin is preferably conducted in the presence of only small amounts of water. This may, for example, be accomplished by adding epichlorohydrin to the aqueous reaction mixture containing the phenolic material as described above, allowing the mixture to form an aqueous and organic phase and then discarding the aqueous phase.

The amount of the polyhydric phenol and the epoxy-forming material to be employed in the reaction will vary depending upon the type of product desired. If simple monomeric type products are desired, the phenol and epoxy-forming material are preferably reacted in mole ratios varying from 1 : 2 to 1 : 10. If higher molecular weight hydroxy-containing products are desired, the epoxy-forming materials are used in smaller amounts and the mole ratio varies from 1 : 1.1 to 1 : 2.

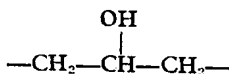
The desired alkalinity is obtained by adding basic substances preferably an alkali hydroxide, such as sodium or potassium hydroxide. The alkali is employed in at least chemical equivalent amount, e.g., one mole of alkali for every phenolic OH group to be reacted and is preferably used in a slight excess up to 5%.

The above reaction is preferably conducted by heating the mixture at temperatures ranging from about 50°C to 150°C and more preferably from about 60°C to 125°C. Atmospheric, superatmospheric or subatmospheric pressures may be utilized as desired.

The water formed in the reaction may be removed during or at the end of the reaction. At the completion of the reaction, the water and excess reactants, such as excess epichlorohydrin are preferably removed by distillation and the residue that remains then treated with an appropriate solvent, such as benzene, and filtered to remove the salt. The product that remains may then be purified by any suitable method, such as extraction, distillation, and the like.

The new epoxy ethers of the present invention are fluid or viscous liquids to solids. They have more than one epoxy group per molecule and are substantially free of chlorine, i.e., contain less than 1% to 2% chlorine. In addition to the active epoxy groups, the new ethers have at least one highly reactive methylol group which may undergo further reaction. The new epoxy ethers are in general soluble in most solvents, such as ketones, alcohols and liquid hydrocarbons and are compatible with many synthetic oils and resins.

For certain applications it is sometimes desirable to have higher molecular weight epoxy resins. Such products may be obtained by varying the amount of the methylol-substituted 2,2 - bis(4 - hydroxyphenyl)propane and epichlorohydrin in the alkaline medium as described above, or by reacting a diglycidyl ether of methylol-substituted 2,2 - bis(4 - hydroxyphenyl)propane with a less than equivalent amount of 2,2 - bis(4 - hydroxyphenyl)propane. In this case the phenolic hydroxyl groups react with epoxy groups to form



groups.

The new epoxy ethers and their higher molecular weight derivatives may be polymerized through the epoxy group to form valuable polymeric products. They may be polymerized alone or with other polyepoxide materials in a variety of different proportions, such as, for example, with amounts of other polyepoxides varying from 5% to 59% by weight. Polyepoxides that may be copolymerized with these new epoxides include, among others, glycidyl polyethers of polyhydric phenols obtained by reacting polyhydric phenols, such as bisphenol, resorcinol, and the like, with an excess of chlorohydrin, such as epichlorohydrin, polyepoxide polyethers obtained by reacting an alkane polyol, such as glycerol and sorbitol, with epichlorohydrin and dehydrohalogenating the resulting product, polymers prepared from ethylenically unsaturated epoxides, such as allyl glycidyl ether, alone or with other ethylenically unsaturated monomers, and polyepoxide polyethers obtained by reacting a polyhydric alcohol or polyhydric phenol with any of the above-described polyepoxides. The glycidyl polyethers of polyhydric phenols obtained by condensing the polyethers of polyhydric phenols with epichlorohydrin as described are also referred to as "ethoxyline" resins.

A great variety of different curing agents may be employed in effecting the above-

described homo- and copolymerization. Such agents include, among others, carboxylic acids or anhydrides, such as oxalic acid, phthalic anhydride; Friedel Crafts metal halides, such as aluminium chloride, zinc chloride, ferric chloride or boron trifluoride as well as complexes thereof with ethers, acid anhydrides, ketones, diazonium salts, phosphoric acid and partial esters thereof including *n* butyl orthophosphate, diethyl orthophosphate and hexaethyl tetraphosphate; amino compounds, such as triethylamine, ethylene diamine, diethylamine, dicyandiamide, melamine; and salts of inorganic acids, such as zinc fluoborate, potassium persulphate, nickel fluoborate, copper fluoborate, selenium fluoborate, magnesium fluoborate, tin fluoborate, potassium perchlorate, cupric sulphate, cupric phosphate, cupric phosphite, magnesium arsenate, magnesium sulphate, cadmium arsenate, cadmium silicate, aluminium fluoborate, ferrous sulphate, ferrous silicate, manganese hypophosphite, nickel phosphate and nickel chlorate, hydrazides, polymercaptans, urea formaldehyde and phenol formaldehyde condensates and the like and mixtures thereof.

Examples of other curing agents include the aromatic amines, such as, for example, diaminodiphenylmethane, *p,p'*-aminodiphenylsulphone, triaminobenzene, ortho-, meta- and paraphenylene diamine, methylene dianiline, diaminotoluene, diamino-diphenyl, diaminostilbene, 1,3-diamino-4-isopropylbenzene, and 1,3-diamino-4,5-diethylbenzene and the like, and mixtures thereof.

Examples of other curing agents include the amino hydrogen-containing polyamides, obtained from polymeric unsaturated fatty acids such as dimerized or trimerized linoleic acid by reacting them with aliphatic polyamines such as diethylene triamine, triethylene tetramine and the like. Other examples include the *N*-aminoalkylpiperazines, such as *N*-aminoethylpiperazines, the acetone-soluble adducts of monoamines, the acetone-soluble adducts of polyamines and unsaturated nitriles, aliphatic polyamines of the formula



wherein *R* is an alkylene radical and *n* is an integer of at least one, such as diethylene triamine, triethylene tetramine, tetraethylene pentamine and the like, as well as other amines, such as *N,N'*-diethyl-1,3-propanediamine, tetra(1,3-dimethylpropylene)-pentamine and the like.

Other examples include the anhydrides, such as tetrahydrophthalic anhydride, methyl Nadic anhydride (Nadic is a Trade Mark), chlorendic anhydride, pyromellitic anhydride, trimellitic anhydride, phthalic anhydride, succinic anhydride, maleic anhydride, octadecenylsuccinic anhydride and the like, and mixtures thereof.

Other examples include the boron trifluoride complexes with aliphatic or aromatic amines such as  $BF_3$ -ethylamine,  $BF_3$ -diethylamine,  $BF_3$ -aniline addition products and the like.

The amount of the curing agents employed may vary over a considerable range depending upon the agent selected. With catalytic-type curing agents one preferably employs from about 0.1% to 10% by weight of the material being cured. With curing agents having replaceable hydrogen, such as the amine agents, which enter the reaction, amounts of agent employed vary from about 0.6 to 1.5 equivalent proportions, i.e., an equivalent proportion being sufficient curing agent to furnish a replaceable hydrogen atom for every epoxy group to be reacted. In general, satisfactory cures are obtained with amounts varying from 1% to 25% by weight of the material being polymerized.

The epoxy ethers and their high molecular weight derivatives may also be cured through the hydroxy group by the addition of appropriate amounts, e.g., 1% to 25% by weight of polybasic acids or anhydrides or polyisocyanates.

The curing is preferably effected by mixing the curing agent with the epoxy ether at temperatures ranging from about 0°C to 200°C. The curing is accelerated by heat and when fast cures are desired, temperatures ranging from about 50°C to 200°C are used. However, as noted above, one of the great advantages of the new epoxy compounds is their ability to cure at low temperatures. In this case, the cure is preferably effected at temperatures of about 0°C to 60°C and still more preferably at 20°C to 50°C.

In some cases, and particularly in the preparation of castings, the new epoxy ethers will be soft to brittle solids and it may be advantageous to employ some type of diluent during their utilization. These diluents are preferably of the reactive type, i.e., those which may enter the reaction. Examples of these include the monoglycidyl compounds, such as the alkyl glycidyl ethers as butyl glycidyl ethers or aryl glycidyl ethers as phenyl glycidyl ether. Other examples include the glycidyl ethers of dihydropyranalkanols, acetonitrile, acrylonitrile, as well as fluid polyepoxide materials such as diglycidyl

aniline. These materials are preferably used in amounts from about 0.1% to as high as or higher than 30% by weight.

It was surprisingly found that with many of the above-noted diluents, the diluent in moderate amount does not destroy any of the superior properties but permits such properties to be obtained without any detrimental effect. This is shown in the examples at the end of the specification.

If the epoxy ethers and their higher molecular weight derivatives are to be used in the preparation of castings or pottings, the curing agent and the epoxy material are generally combined together and then poured into the desired mould or casting containing the electrical wires or apparatus and the mixture heated to effect the cure.

The new epoxy ethers of the invention and their higher molecular weight derivatives are particularly suitable, because of their fast rate of cure at the lower temperatures, for the preparation of surface coating compositions. In utilizing the products for this application, it is generally desirable to combine the epoxy resin and curing agent with the desired solvent or diluent, and, if desired, other film-forming materials, extenders, fillers or driers, and then apply the resulting mixture to the surface to be coated. Film-forming materials that can be used with the epoxy material in this manner include the drying oils, such as tung oil, linseed oil, dehydrated castor oil, soyabean oil and the like; cellulose derivatives such as cellulose nitrate, cellulose acetate, cellulose acetate butyrate, ethyl cellulose and mixtures thereof; the vinyl polymers, such as polymers of vinyl chloride, vinylidene chloride, acrylonitrile, acrylates, diallyl phthalate, ethylene, propylene, butylene, rubbery polymers from butadiene and isoprene and the like; coal tars, pine oils, and asphalts and other types of bituminous materials. The coatings prepared in this manner may be allowed to set hard at room temperature or heat may be applied to hasten the cure.

The higher molecular weight hydroxy-containing derivatives of the epoxy resin as described above are particularly suited for use in preparing coating compositions as they may be reacted through the hydroxyl group or groups with drying oil fatty acids or may be cured through the hydroxyl groups with compounds such as urea or polyisocyanates.

The new epoxy resins and higher molecular weight derivatives may also be employed with appropriate curing agents in the preparation of valuable adhesives and laminating compositions. In utilizing the products in these applications, it is generally desirable to combine the epoxy resins with fillers and curing agents and then use the spreadable fluid as adhesive for materials, such as wood, plastic, metal and the like.

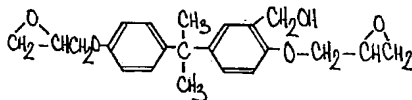
In addition, the new epoxy ethers may be used as stabilizing agents for various halogen-containing polymers, and particularly the vinyl halide polymers. These products may be used as stabilizers, alone or in combination with other stabilizing agents, such as urea and thiourea derivatives. In most cases, the products are effective as stabilizers in amounts varying from 1% to 5% by weight of the polymer being stabilized. The epoxy materials may be combined with the halogen-containing polymer by any suitable method, such as by dissolving the products in a suitable solvent or by milling the products together on a suitable roll mill.

The new epoxy ethers are particularly attractive for use in aqueous systems where the methylol group or groups facilitate the dissolution or emulsion of the resin in the water. This makes the new ethers of value in making water-based coating compositions, adhesives, impregnating compositions, solutions for treating cloth, paper, leather and the like, to impart improved properties thereto.

To illustrate the manner in which the invention may be carried out the following examples are given. It is to be understood that the examples are for the purpose of illustration and the invention is not to be regarded as limited to any of the specific compounds or conditions recited therein. Unless otherwise specified, parts disclosed in the examples are parts by weight.

#### EXAMPLE I

This example illustrates the preparation and some of the properties of a monomethylol-substituted diglycidyl ether of 2,2-bis(4-hydroxyphenyl)propane having the structure



46 parts (0.2 mol) of 2,2 bis(4 hydroxyphenyl)propane were dissolved in 25.4 part of methanol and to this mixture were added 18 parts (0.222 mol) of a 37% formalin solution, and 21.5 parts (0.1 mol) of a 20% aqueous sodium hydroxide solution. This mixture was heated for about 20 minutes at 82° C. The reaction mixture was then neutralized with dilute sulphuric acid and the methanol removed by distillation. A ten molar excess of epichlorohydrin was then added to the reaction mixture and the mixture stirred at room temperature. The combined mixture was then allowed to stand at room temperature until the water phase had separated. The organic phase was then removed and combined with 25% by weight of methanol. This solution was heated to reflux and concentrated sodium hydroxide solution added to give 5% excess based upon the phenol. At the conclusion of the reaction, the excess epichlorohydrin and methanol were removed. The resulting product was then dissolved in methyl isobutyl ketone and filtered to remove the salt. The mixture was then stripped at 150°C at 2 mm to remove the ketone solvent and yield the desired viscous thick substantially colourless resin having the structure noted above. Analysis indicated the product had an epoxy value of 0.44 eq/100 g, a hydroxyl value of 0.297 eq/100 g, chlorohydrin value of 0.118 eq/100 g, chlorine value of 1.1%w and a molecular weight of 428 ± 20. Calc. values are epoxy 0.54 eq/100 g, hydroxyl 0.27 eq/100 g, mol weight 370.

#### EXAMPLE II

This example illustrates the rapid rate of cure obtained with the new methylol-substituted epoxy ethers.

100 parts of the methylol-substituted glycidyl ether produced in the preceding example were combined with 10.9 parts of diethylene triamine. The disappearance of epoxy groups was determined against time at 75°F by near infrared spectography and the results plotted on the graph shown in Figure 1 (line A) in which the abscissae are the hours at 75°C and the ordinates are the epoxide content as a percentage of the original. Similar results were determined for a related mixture prepared from the unsubstituted glycidyl ether and the diethylene triamine. The results in this latter case are shown in line B. An examination of the graph clearly illustrates the rapid rate of cure (disappearance of epoxy groups) obtained with the new methylol-substituted glycidyl ethers.

#### EXAMPLE III

This example also illustrates the rapid rate of cure obtained with the new methylol-substituted epoxy ethers.

The monomethylol-substituted glycidyl ether produced in Example I was combined with 8.7 parts (per 100 parts of ether) of diethylene triamine and 80 parts of dioxane and the mixture cured at room temperature. The gel time for this mixture was 1.0 hours. In a related experiment using 11.4 parts of the diethylene triamine with the glycidyl ether of the unsubstituted bis-phenol, the gel time was 8.4 hours.

The above experiment was prepared at 50°C. The unsubstituted ether had a gel time of 25 minutes while the new methylol-substituted ether had a gel time of only 3 minutes.

A 50—50 mixture of the unsubstituted glycidyl ether and the methylol-substituted glycidyl ether produced in Example I cured with 10 parts of diethylene triamine and no solvent in 7 minutes.

#### EXAMPLE IV

100 parts of the methylol-substituted glycidyl ether produced in Example I were combined with 6 parts of diethylene triamine and the mixture spread out as a thin film and cured at room temperature. The results are compared with those obtained from a similar film prepared from diethylene triamine and the unsubstituted glycidyl ether:

	Monomethylol-substituted	Unsubstituted
Drying Time (set to touch)	10 minutes	45 minutes
Dry hard	2.5 hours	3.5 hours
Solvent Resistance — 15 minutes contact with Methyl Ethyl Ketone after 24 hours cure	No effect	Very soft

The above experiment was repeated with the exception that the cure was accom-

plished at a lower temperature (40°F). The film set to touch at 1.5 hours and was dry hard at 7.5 hours. Cures at this lower temperature also gave a product which had improved flexibility and impact resistance.

#### EXAMPLE V

The monomethylol-substituted glycidyl ether produced in Example I was combined with 11.3 parts of meta-phenylene diamine and the mixture heated at 200°C for about 4 hours. The resulting product was a hard insoluble infusible casting having a heat distortion point of 260°C. If the heating were continued to 5 to 6 hours, the heat distortion point would be around 300°C.

In a related experiment, the diglycidyl ethers of the unsubstituted 2,2-bis(4-hydroxyphenyl)propane was combined with 14 parts of meta-phenylene diamine and heated for 4 hours at 200°C. In this case, the casting had a heat distortion point of only 150°C. In a further experiment, a glycidyl ether of an unsubstituted phenolformaldehyde resin was combined with 16 parts of metaphenylene diamine and heated as above. The product in this case had a heat distortion point of 190°C.

A comparison of the above results clearly indicates the unexpected superior improvement obtained in heat resistance by the use of new epoxy ether of the invention.

#### EXAMPLE VI

The monomethylol-substituted glycidyl ether produced in Example I was combined with each of the following: 89 parts (per 100 of resin) of Nadic methyl anhydride (methyl-endomethylene-tetrahydrophthalic anhydride) and one part of benzyldimethylamine, and an equivalent amount of hexahydrophthalic anhydride and 1 part of benzyldimethylamine. The mixtures were heated to 150°C. The resulting castings are hard insoluble infusible products having high heat distortion points.

#### EXAMPLE VII

The monomethylol-substituted glycidyl ether produced in Example I was combined with various proportions of the following components and cured in the presence of equivalent amounts of diethylene triamine; 10% refined coal tar, 20% middle oil, 15% high aromatic petroleum derived oil, 25% pine oil. The resulting products are hard tough castings.

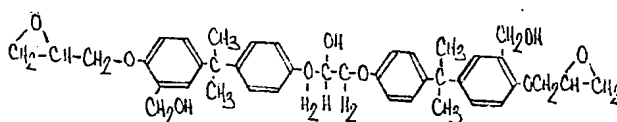
#### EXAMPLE VIII

This example illustrates the preparation and properties of a tetramethylol-substituted diglycidyl ether of 2,2-bis(4-hydroxyphenyl)propane.

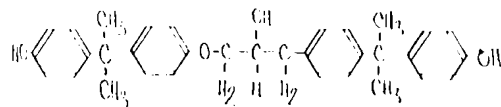
457 parts of 2,2-bis(4-hydroxyphenyl)propane were dissolved in 300 parts of methanol and to this mixture were added 400 parts of a 37% formalin solution, 47 parts of 20% aqueous sodium hydroxide solution and 300 parts of water. This mixture was allowed to stand at room temperature for six days and then 320 parts of a 37% formalin solution were added and the mixture allowed to stand for an additional eight days. This mixture was neutralized with dilute sulfuric acid and then distilled to remove the methanol. A ten molar excess of epichlorohydrin was added and the mixture stirred at room temperature. The mixture was allowed to stand until the water phase separated. The organic phase was removed and combined with 25% by weight of methanol. The solution was heated to reflux and concentrated caustic was added to give 5% excess based upon the phenolic hydroxyl content. At the end of the reaction, the excess epichlorohydrin and methanol were stripped off at 125–130°C at 25 mm. The product was dissolved in methyl isobutyl ketone, filtered to remove the salt and stripped at 130°C at 2 mm to give a soft solid resin having about four methylol groups per bisphenol group. The product had an epoxy value of 0.25eq/100g, OH value 0.77 eq/100 g.

#### EXAMPLE IX

This example illustrates the preparation and some of the properties of a dimethylol substituted diglycidyl ether of the following formula



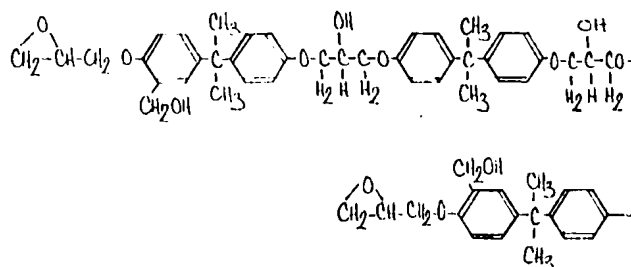
A polyhydric phenol containing 2 units of the 2,2 - bis(4 - hydroxyphenyl)propane was prepared by dissolving 228 parts of 2,2 - bis(4 - hydroxyphenyl)propane in 200 parts of methanol and to this mixture were added 46 parts of epichlorohydrin, 25 parts of 20% aqueous sodium hydroxide and 25 parts of water. The solution was refluxed for 2 hours at 74°C after which the temperature was raised to 150°C by removing the solvent. The product formed by this reaction had the formula



To the above described reaction mixture were added 85 parts of 37% formalin solution, 25 parts of 20% aqueous sodium hydroxide and 25 parts of water and 20 parts of methanol. This mixture was refluxed at 76°C for 1/2 hour. The mixture was then neutralized with 15% sulphuric acid and the methanol stripped off. 840 Parts of epichlorohydrin were used to dissolve the resin and the mixture was allowed to stand until an aqueous and organic phase separated. The organic phase was removed and combined with 150 parts of methanol and 40 parts of concentrated sodium hydroxide solution. This mixture was refluxed for 1/2 hour and the solvents were removed at 120°C at 23 mm. The resulting product which was a mixture of resin and salt was dissolved in 500 parts of methyl ethyl ketone and filtered. The filtrate was stripped at a temperature of 140°C/2 mm Hg to remove the solvent. The resulting product was a hard solid resin having the above structure and an epoxy value of 0.26 eq/100 g, hydroxyl value 0.49 eq/100 g and a molecular weight of 620. The calculated values are: epoxy value 0.40 eq/100 g, hydroxy value 0.44 eq/100 g, and mol weight at 684.

#### EXAMPLE X

This example illustrates the preparation and properties of a dimethylol substituted diglycidyl ether of 2,2-bis(4-hydroxyphenyl)propane having the structure



228 parts of 2,2 - bis(4 - hydroxyphenyl)propane, 170 parts of diglycidyl ether of 2,2 - bis(4 - hydroxyphenyl)propane and 175 parts of methanol were combined together and 2 parts of potassium hydroxide added at room temperature. The mixture was heated to 145°C for one hour and the methanol was removed by distillation. The resulting product was a polyhydric phenol of the above structure free of the epoxy ether groups and free of methylol groups.

175 parts of methanol were added to the reaction mixture along with 85 parts of 37% formalin, 30 parts of sodium hydroxide and 50 parts of water. This mixture was refluxed for 1/2 hour. The mixture was neutralized with sulphuric acid and the methanol removed by distillation. A ten molar excess of epichlorohydrin was then added and the product allowed to stand at room temperature. The mixture separated into an aqueous and organic phase and the organic phase was removed and combined with 25% by weight of methanol. This mixture was heated to reflux and 5% excess of concentrated sodium hydroxide added. At the completion of the reaction the excess epichlorohydrin and methanol were stripped at 125-130°C at 25 mm leaving a desired resin salt mixture. The product was dissolved in methyl ethyl ketone, filtered and then stripped to yield the desired resin. The resulting product had the above-described structure and had an epoxy equivalency of 0.188 eq/100 g.

## EXAMPLE XI

The polyepoxide resins produced in Example I, VIII to X, were combined with equivalent amounts of each of the following epoxy curing agents: dicyandiamide, diethylene triamine, boron trifluoride-ethyl amine complex, ethyl maleic anhydride, meta-diphenylene, diamine and a polyamide of dimerized linoleic acid and ethylene diamine. In each the resulting mixtures were heated at 100°C for several hours. In each case hard clear resins were obtained.

## EXAMPLE XII

The monomethylol-substituted diglycidyl ether of 2,2 - bis(4 - hydroxyphenyl)propane produced in Example I was combined with a variety of different proportions of butyl glycidyl ether. The viscosities of the resulting solution are shown in the attached drawing, Figure II under line A in which the abscissae are the weight per cent of diluent and the ordinates are the Brookfield viscosity in poise at 25°C. Each of these low viscosity solutions was combined with an equivalent amount of meta-phenylene diamine and cured at 100°C. The resulting products are hard tough insoluble castings which possess outstanding heat distortion points.

## EXAMPLE XIII

The monomethylol-substituted glycidyl ether of 2,2 - bis(4 - hydroxyphenyl) propane produced in Example I was also combined with various proportions of glycidyl ether of dihydropyran-2-methanol. The viscosities of the resulting solutions are shown in the attached drawing, Figure II under line B. Each of these low viscosity solutions was combined with an equivalent amount of meta-phenylene diamine and cured at 100°C. The resulting products are hard tough resins having heat distortion points.

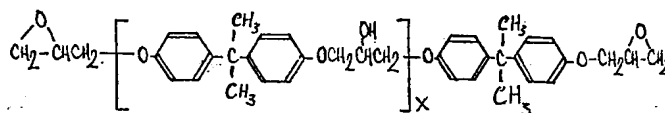
## EXAMPLE XIV

100 parts of the monomethylol-substituted glycidyl ether produced in Example I were combined with 50 parts of an amino-containing polyamide of dimerized linoleic acid and diethylene triamine. The mixture was spread out as a film and cured at 4°C and another set at 24°C. The results are shown below:

	4°C Cure	24°C Cure	
Drying Time		25 minutes	40 minutes
set to touch			
Dry Hard		7.5 hours	2 hours
Flexibility, mandrel		passed $\frac{1}{8}$ inch	passed $\frac{1}{8}$ inch
Pencil Hardness		HB	HB
Solvent Resistance			
Methyl isobutyl ketone		no effect	no effect
xylene		" "	" "
water (cold—15minutes)		" "	" "

## WHAT WE CLAIM IS:—

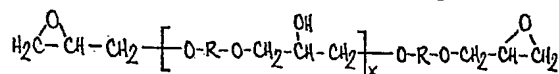
1. As a novel compound a polyglycidyl ether of the formula:



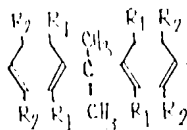
wherein x is an integer from 0 to 10 and at least one of the p-phenylene radicals is substituted with a methylol group, no other substituents being present.

2. A glycidyl ether as claimed in claim 1 in which x is from 0 to 5.
3. A glycidyl ether as claimed in claim 1 or 2, having from 1—4 methylol groups per molecule.

4. A glycidyl ether as claimed in any of the preceding claims having the formula:

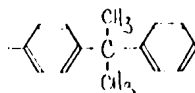


wherein R is a bivalent



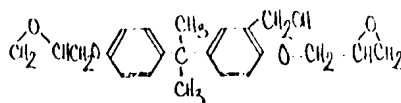
group, wherein  $R_1$  and  $R_2$  are hydrogen or methylol groups, and  $x$  is a number from 0 to 10, with the proviso that in at least one  $R_1$  is a methylol group.

5. A glycidyl ether as claimed in claim 4, wherein  $x$  in the molecular formula is a number from 0 to 5 and each  $R$  is a methylol substituted



group.

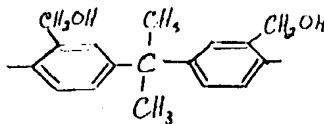
6. As a novel compound a glycidyl ether of the formula:



10

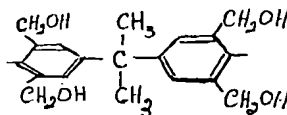
7. A glycidyl ether as claimed in claim 4 in which  $R$  is a

10



group.

8. A glycidyl ether as claimed in claim 4 in which  $R$  is a



15

group.

15

9. A process for the preparation of a glycidyl ether as claimed in any one of claims 4 to 8, which comprises reacting a 2,2 - bis(4 - hydroxyphenyl)propane substituted on an aromatic ring with as only substituent at least one methylol group per molecule with epichlorohydrin or  $\alpha$ -dichlorohydrin in a mole ratio of at least 1:1.1 in the presence of an alkaline material.

20

20

10. A process as claimed in claim 9, wherein the mole ratio of methylol-substituted 2,2 - bis(4 - hydroxyphenyl)propane to epichlorohydrin or  $\alpha$ -dichlorohydrin is from 1:2 to 1:10.

25

25

11. A process as claimed in claim 9, wherein the mole ratio of methylol-substituted 2,2 - di(4 - hydroxyphenyl)propane to epichlorohydrin or  $\alpha$ -dichlorohydrin is from 1:1.1 to 1:2.

12. A process as claimed in any one of claims 9 to 11 wherein the alkaline material is an at least chemical equivalent amount of an alkali hydroxide based on the phenolic-hydroxyl content.

13. A process as claimed in any one of claims 9 to 12, wherein the reaction is conducted at temperatures from 50°C to 150°C.
14. A process as claimed in any one of claims 9 to 13, substantially as described in any of the Examples I and VIII.
- 5 15. A process for the preparation of a compound as claimed in claim 1 substantially as described in Example IX or X. 5
16. Glycidyl ethers, substantially as described in any of the Examples I and VIII to X.
- 10 17. A process for curing a glycidyl ether according to any one of claims 1 to 8 and 16 which comprises reacting the glycidyl ether with an epoxy curing agent of the group consisting of amines, amino groups containing polyamides, polycarboxylic acids and their anhydrides, boron trifluoride and its complexes, metal salts of inorganic acids, hydrazides, polymercaptans, urea-formaldehyde and phenol-formaldehyde condensates. 10
- 15 18. A cured product obtained by the process as claimed in claim 17.
19. A cured product obtained by reacting a mixture containing a glycidyl ether according to any one of claims 1 to 8 and 16, and a dissimilar polyepoxide with an epoxy curing agent of the group defined in claim 17. 15
- 20 20. A cured product obtained by reacting a mixture containing a glycidyl ether according to any one of claims 1 to 8 and 16, and a monoglycidyl ether diluent with an epoxy curing agent of the group defined in claim 17. 20
21. A cured product, substantially as described in any one of the Examples II to VII and XI to XIV. 20
22. A laminate comprising a product as claimed in any one of claims 18 to 21.

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COMPLETE SPECIFICATION

1 SHEET

*This drawing is a reproduction of  
the Original on a reduced scale*

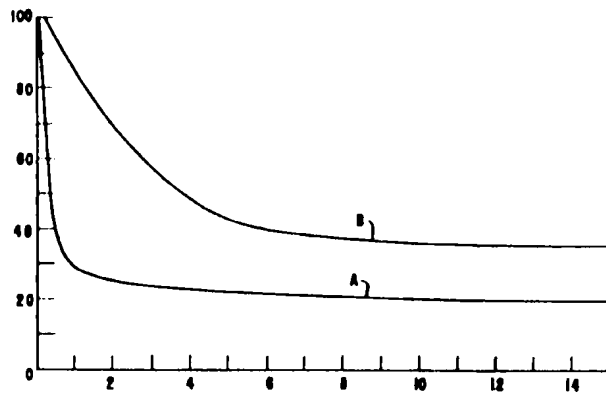


FIG. I

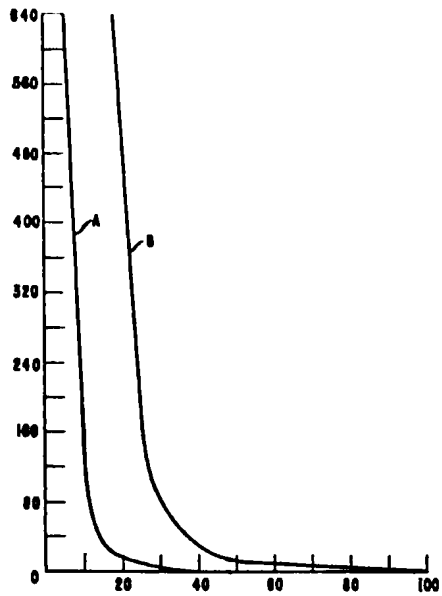


FIG. II